10/018088
PCT/FI00/00532

1/pts

JC13 Rec'd PCT/PTO 14 DEC 2001

Method to improve the opacity of mechanical pulp by using aliphatic peroxyacids and use of peroxyacids to improve opacity.

The invention relates to a process for treating mechanical pulps, which can be used to affect the opacity of the pulp.

The nontransparent aspect of paper is described by opacity, which, along with brightness, is an important property of pulp in paper manufacture. Almost invariably, however, the opacity of the pulp decreases when the brightness increases. At present, mechanical pulps (refiner mechanical pulp, groundwood pulp, and chemimechanical pulp) are more and more often bleached with hydrogen peroxide. Dithionite bleaching is also used either alone or together with peroxide bleaching, whereupon dithionite is either used as refiner bleaching or after-bleaching. In the peroxide bleaching of pulp, mechanical pulp in particular, the decrease of opacity is clearly detectable, while the dithionite bleaching does not necessarily decrease the opacity. Generally, the lighter the level of bleaching the pulp, the lower the opacity of the pulp. The appended Fig. 1 that shows a variation in the opacity of spruce TMP, when peroxide is used to bleach pulp to various degrees of brightness manifests this. In certain paper grades, opacity is an important property. If we want to advance peroxide bleaching at the expense of dithionite bleaching, it would be important to be able to optimize peroxide bleaching so that the opacity remains as high as possible while the brightness grows.

Generally, the chemicals used in the peroxide bleaching of mechanical pulps are hydrogen peroxide, lye (alkali), and waterglass. The purpose of the base is to increase the pH to a sufficiently high level, so that the hydrogen peroxide is dissociated producing perhydroxyl anions. The purpose of the waterglass is to stabilize the hydrogen peroxide bleaching.

It is well known that peracetic acid can be produced in situ, for example, from acetanhydride or TAED (tetra acetyl ethylene diamine) or some other corresponding activator. One disadvantage of TAED is its high price and that it is a solid substance. It would be necessary to disperse the TAED in water before adding it to the pulp, which makes it difficult to use. Furthermore, TAED contains nitrogen, which might constitute a problem for environmental protection. Acetanhydride is relatively cheap, but it would cause odour nuisance and be an inconvenient substance from the point of view of industrial safety. In addition, when fed into an alkaline bleaching solution (NaOH + H_2O_2 + waterglass), it would readily cause silicate precipitate and consume the lye.

Paper manufacture aims at ever-higher brightness levels. The brightness of paper can be affected, for example, by treating the paper with coating agents containing, among other things, pigments, binding agents, and plasticizing agents (JP application 284598).

However, the use of several coating agents at the final stage of paper manufacture adds to the manufacturing costs.

The agent that affects the opacity of a technically useful pulp should be liquid and stable, and it should preferably have a suitable pH value, so that no silicate precipitate would form in the bleaching. Because of environmental matters, a nitrogen-free substance would provide an additional benefit. The additive of the bleaching should also be cost-effective for the paper manufacturers. Consequently, a substance should be found for pulp bleaching, which, to fulfil the conditions mentioned above, is a reasonable, commercial chemical that is easy to get and can be added to the pulp as early as at the bleaching stage. Furthermore, attention should also be paid to the other effects of the substance, such as applicability in plant conditions.

The purpose of this invention is to find a useful substance that is used in pulp bleaching and that affects the opacity, fulfilling the conditions mentioned above.

The main features of the invention are disclosed by the appended Claims.

Surprisingly, we have now observed that, when a small portion of peracid is either added to the peroxide bleaching or with the purpose of finishing the peroxide bleaching, the opacity of pulp improves compared with pulp of a corresponding brightness level that is bleached with hydrogen peroxide alone. At the same time, we have observed that peracids scarcely increase the brightness.

The use of peracetic acid in bleaching chemical pulps is disclosed by the published Japanese application JP 57-21591, for example. However, bleaching processes like this aim at removing the lignin from the pulp and, in this case, the purpose is in no way to adjust the opacity of the pulp.

Tappi publication, Vol. 48, No. 2 (2/1965), W.H. Rapson et al. Paper Bleaching – A New Process, pp. 65-72, discloses a method for bleaching paper by using peracetic acid, among others. However, this method does not aim at improving the opacity of pulp, but increasing the brightness. Furthermore, the disclosed method uses considerable amounts of peracetic acid, about 1.2 – 2.5% (i.e., 12-25kg/ton of pulp). Such a portion can dissolve a considerable amount of lignin etc. from the pulp, whereupon the paper manufacturing process can be severely disturbed. The publication also reveals that the technical performance of the method deviates from our invention.

The use of peracids as a biocide is also disclosed by publication Kemia, No. 3 (1995), Jyri Maunuksela, Mikrobien torjunta peretikkahapolla (Microbe Prevention with Peracetic Acid), pp. 242-244. Such a method aims at destroying microbe populations in the paper machine only. It is self-evident that peracetic acid, which is known to be an effective biocide, prevents the functioning of microbes in the water circulation, if a sufficient amount is present. The method disclosed by the publication uses a so-called equilibrium peracetic acid that contains a considerable amount of free acetic acid and hydrogen peroxide. The acetic acid and hydrogen peroxide that come with the peracid can disturb the paper manufacturing process.

Bleaching methods based on peracetic acid have also been presented, aiming at improving the brightness of the pulp compared with normal bleaching methods. Such a method is presented, for example, by publication Pulp and Paper Magazine of Canada, Convention Issue, 1972, pp. 123-131, and by number 3/1968 of the same magazine in pages 51-60. The doses of peracid used by these methods are very high and, consequently, dissolve a considerable amount of lignin from the surfaces of the fibres. In addition, these methods aim at increasing the brightness of the pulp, i.e. at bleaching.

One difference between the treatments mentioned above and our invention in particular is that the peracid treatments implemented by the means disclosed by them fail to improve the opacity of the pulp; none of the publications mentioned above tried to achieve a considerable increase in the opacity either.

The invention relates to a method, in which the peracid is either added to the peroxide bleaching or, preferably, after the peroxide bleaching, either to the storage tower of the bleached pulp or, for example, among the machine pulp in the paper machine. Typically, the amount of peracid added to the pulp is about 1-3 kg/ton of pulp. Because of its small amount, the peracid does not dissolve the lignin or the like from the pulp, whereupon it does not disturb the paper manufacturing process. It is especially advantageous to use peracid solutions, which have been purified, so that they mainly contain the peracid in question and water only. In that case, the addition of peracid does not have a considerable effect on the pH value of the stock, and no extra COD gets into the process. The invention differs from the known methods based on peracid namely in that it does not aim at increasing the brightness but growing the opacity. A matter worth noticing in particular is that the method differs from the known bleaching treatments also in that the peracid doses used are very small and the method tries to avoid the dissolution of organic matter from the fibres.

The method is not actually a bleaching method, and the chemicals used in the actual bleaching of the pulp have no effect whatsoever on the functioning of the invention.

The pulp can be bleached with dithionite, peroxide, dithionite and peroxide, or it can even be completely unbleached. Any chelation agents or other additives used in pulp manufacture have no effect on the functioning of the invention either.

The consistency of the pulp at the moment the peracid is added can be 1-40%; the temperature can be 20-100°C. Depending on the process, the pH of the stock can be 3-11, preferably 4-8. If the peracid is added to alkaline peroxide bleaching, an advantageous pH value is 9-11, however. A suitable reaction time for the peracid is 1-300 minutes depending on the process.

The method is well suited to the treatment of mechanical pulp, such as groundwood pulp (SGW, PGW) and refiner mechanical pulp (TMP), or to treat chemi-mechanical pulps (CTMP). The sort of wood used to manufacture the pulp has no importance to the functioning of the invention.

A suitable dose of peracid has been found to be 0.5-5 kg/ton of pulp, typically 1-3 kg/ton of pulp. The peracid used can be any peracid that reasonably dissolves in water. We have noticed that peracetic acid and perpropionic acid are preferable peracids, and especially preferable are the peroxide-free distillates that are prepared from the equilibrium solutions of these. The manufacturing method of peracid has no effect on the functioning of the invention. Peracid solutions that are either purified by distillation or some other method, or the equilibrium solutions of peracids can be used as peracid. Various mixtures of peracids are also usable. One modification of the invention can use a mixture of peracid and Caro´s acid.

Example 1

CTMP pulp was bleached with peroxide in a normal manner. Peracids were added to the bleaching solution, the results are shown in Table 1.

Table 1

CTMP, bleaching solution: NaOH 24 kg +waterglass 20 kg + H_2O_2 30 kg/ton of pulp, 70°C, consistency 30%, 120 min, chelated pulp, peracid added to the bleaching, PAA = peracetic, PPA = perpropionic acid

	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	78.4	64.9
PAA	2	79.1	67.2
PPA	2.2	78.3	70.7

The results show that, by using peracids, a distinctly higher opacity with the same brightness level is achieved than by using peroxide bleaching alone.

Example 2

Bleached CTMP pulp was treated with peracids, the results are shown in Table 2.

Table 1

Bleached CTMP

After-treatment

t = 50°C, 30 min, pH 7, consistency 5%

	Dosage, kg/ton of pulp	Brightness, % ISO	Opacity
None	-	65.9	71.5
PAA	2	66.6	74.1
PPA	2.2	65.8	74.3

The results show that an after-treatment has an obvious effect on the opacity.

Example 3

So-called machine pulp taken from the plant and containing 16% of softwood pulp, 64% of TMP pulp, and 20% of coated broke (the basic pulp mixture was softwood: TMP 20:80) was treated with peracetic acid. The softwood pulp was normal ECF sulphate pulp. The TMP had been bleached with dithionite. The results are shown in Table 3.

Table 3

	Pulp mixture:	
Machine pulp	Softwood pulp	16%
	TMP	64%
	Coated broke	20%

30 min, 70°C, Cs 3.2%, (the test was conducted by using the water of the plant)

No.	PAA, kg/ton of pulp	pH	TOC, kg/ton of pulp	Brightness, % ISO	Opacity, %	Note!
0	0	5.0	10.4	71.9	91.3	Untreated
1	0	4.9	9.6	71.6	91.8	30 min, at 70°C
2	1	4.6	8.9	71.7	96.5	Distilled PAA
3	2	4.6	9.6	71.9	95.8	Distilled PAA
4	4	4.2	10.2	71.3	96.9	Distilled PAA
5	2	4.5	11.0	70.7	97.1	Equilibrium solution
6	1	5.0	9.5	71.6	93.7	Distilled PAA
7	2	4.9	10.3	71.5	94.4	Distilled PAA
8	2	5.0	10.1	68.8	93.4	Equilibrium solution

Distilled PAA = 38% of PAA, 1% of H_2O_2

Equilibrium solution = PAA 13%, acetic acid 22%, H_2O_2 15%

The results show that the opacity grew considerably because of the treatment with PAA. They also show that the equilibrium solution has an adverse effect on the brightness. The TOC values (total organic carbon) show that the treatment did not dissolve considerable amounts of organic matter from the fibres.